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SUMMARY OF THE TENTH MEETING OF THE REFRACTORY COMPOSITES WORKING GROUP

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Contract No. AF 33(615)-1121
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Roger J. Runck

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Director

TABLE OF CONTENTS

	Page
INTRODUCTION	1
MATERIALS TECHNOLOGY	1
Bulk Refractory Materials	1
Intermetallic Compounds	1
Graphite	1
Metalloids	2
Oxides	2
Mixtures	2
Coated-Refractory Systems	3
Metallic Substrates	3
Coated Graphite	7
Fiber-Reinforced Composites	8
Metal Matrix	8
Oxide Matrix	9
Graphite Matrix	9
Fiber Technology	10
PROCESS TECHNOLOGY	11
SPECIFIC HARDWARE APPLICATIONS	13
Rocket-Motor Components	13
Ablative	13
Radiative	13
Miscellaneous	14
EVALUATION TECHNIQUES	14
Thermal-Testing Facilities	14
Quality Control	15
Miscellaneous	15
APPENDIX A. LIST OF ATTENDEES TO TENTH REFRACTORY COMPOSITES WORKING GROUP MEETING	A-1
APPENDIX B. INDEX OF PAPERS	B-1

SUMMARY OF THE TENTH MEETING OF THE REFRACTORY COMPOSITES WORKING GROUP

E. S. Bartlett and H. R. Ogden*

INTRODUCTION

This memorandum summarizes information on refractory materials and composites that was presented at the Tenth Meeting of the Refractory Composites Working Group. The memorandum is not intended to cover all details of the data reported. Rather, its purpose is to outline current thinking, present highlights of recent advances in composites technology, and identify active programs and organizations.

Most of the data discussed at the subject meeting have been, or will be, contained in readily accessible sources. These include a compilation of the complete reports prepared for this meeting, being prepared for release by the Research and Technology Division of Wright-Patterson Air Force Base.

The Refractory Composites Working Group consists of individuals concerned with design, development, and application of refractory composites for use at temperatures above 2500 F. The group meets at 9-month intervals to exchange current information on refractory composites. Attendance at the Working Group meetings is restricted to organizations active in the field that can freely discuss their work.

The meeting summarized in this memorandum was held at the Georgia Institute of Technology, Atlanta, Georgia, on April 12-14, 1965. Organization and direction of this meeting was accomplished by personnel of the Air Force Research and Technology Division, including Mr. L. N. Hjelm and Lieutenant D. R. James.

The meeting was attended by 68 people representing 58 organizations. A list of the attendees and their organizations is presented in Appendix A. There were 54 oral presentations with open discussion following each talk. Forty-eight of the presentations were supplemented by written reports that were distributed to the attendees. These reports are listed in Appendix B, which also indicates where the information is reviewed in this memorandum.

The information in this memorandum is arranged according to the emphasis given by the reporting organization, in the following four broad categories:

I. Materials Technology
II. Process Technology
III. Specific Hardware Applications
IV. Evaluation Techniques.

Inasmuch as a number of the papers contained information relating to two or more of these categories, this information has been separated and discussed in the appropriate sections of this memorandum.

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Two items receiving particular emphasis at the tenth meeting deserve special comment. Growing interest in the area of fiber-reinforced composites and general fiber technology associated with the composites effort is indicated by the fact that about one-fourth of the presentations dealt with this subject. Accordingly, a separate category, "Fiber-Reinforced Composites", is contained in this summary. The second item involves recurrent comments in the formal presentations and in the discussions relative to the importance of intermediate layers in coated refractory-metal systems in establishing performance of these systems. These sublayers (M_5Si_3, $CbCr_2$, Cr-Ti-Cb-Si, etc.) are now being recognized as contributing important chemical and mechanical characteristics to coated systems, and developments are in progress to better understand their role in the performance of protective coatings.

MATERIALS TECHNOLOGY

Bulk Refractory Materials

Intermetallic Compounds

Continued studies intended to develop refractory intermetallic compounds for application as turbine blades were described by Continental Aviation. Creep and stress-rupture properties of several refractory beryllides were measured at 2200 F:

Compound	Minimum Creep Rate, 10 Ksi, 2200 F, % per hr	100 Hr, 2200 F, Stress Rupture: Strength, ksi	Strength/Density, 10^3 in.
$CbBe_{12}$	0.105	12	114.5
Cb_2Be_{17}	0.105	9	72
$TaBe_{12}$	0.13	7.5	49.5
Ta_2Be_{17}	0.07	15	82
$MoBe_{12}$	1.2	4	35

Based on these data, both $CbBe_{12}$ and Ta_2Be_{17} appear to meet the minimum target requirement of 80,000 inches for rupture strength/density ratio. To investigate the possibility of improving the low-temperature behavior of these brittle materials, Continental considered using either chromium or rhodium as a ductile matrix material. However, preliminary compatibility studies showed neither chromium nor rhodium to be sufficiently inert to the beryllides at elevated temperature.

Graphite

Ling-Temco-Vought, Research Center (LTV Research) has applied highly ordered, dense coatings of graphite to various substrates using an evaporation process. Crystallographic dimensions approaching the ideal parameters for graphite were achieved. In this process, a graphite source rod is heated to 4530 F in vacuum (10^{-5} mm of Hg), and the evaporated carbon is condensed on a substrate held at a temperature "usually less than" 3630 F. Deposits up to 5 mils thick are achieved in 30 minutes at an efficiency of about 30 percent. Total coating thicknesses of up to 40 mils have been prepared in multiple-cycle runs.

Metalloids

A process for vapor deposition of theoretically dense SiC with the β(cubic) structure has been developed by Marquardt. As a free-standing material, this SiC has "excellent thermal-shock resistance", its compressive strength at room temperature exceeds 300,000 psi, and its modulus of rupture is 40,000-50,000 psi. Free-standing bodies are currently being evaluated for rocket thrust-chamber applications.

Properties of hot-pressed metalloid bodies, as reported by Norton, are given in Table 1. Plates in dimensions of 6 by 6 by 1/4 to 1/2 inches, and rings of 1-inch wall thickness and up to 15-inch diameter have been hot pressed.

TABLE 1. PROPERTIES OF CARBON-TITANIUM MIXED BORIDE AS COMPARED WITH THOSE OF ITS COMPONENTS (NORTON)

	B_4C	B_4C/TiB_2(a)	TiB_2
Density, g/ml	2.50	2.89	4.50
Melting point, C	2450	About 2400	2900
Modulus of elasticity, psi	65×10^6	66×10^6	$54\text{-}77 \times 10^6$
Modulus of rupture in bending (RT), psi	40,000	63,000	19,000
Modulus of rupture (2200 F), psi	—	55,000	—
Compressive strength, psi	414,000	600,000	97,000
Knoop Hardness, K_{100}	2,800	2,750	2,710
Thermal conductivity, cal/(sec)(cm^2)(C/cm)	0.065	--	0.060
Electrical resistivity, ohm-cm	0.3-0.8	Low	2×10^{-5}
Coefficient of thermal expansion, C^{-1}	45×10^{-7}	--	--

(a) Mixed boride composition: $80B_4C:20TiB_2$ by volume, 69:31 by weight.

Oxides

Continued research and development on zirconia and alumina rods suitable for flame spraying was described by Norton. By altering rod cross sections to improve flame heating efficiency, 5/16-inch-diameter ZrO_2 rods compatible with the Rokide process will be available during 1965. An increase of 25 percent in coating deposition rate over that obtainable with current 1/4-inch-diameter rods is expected.

Additions of from 1/4 to 3/4 percent of $Al_2(OH)_5Cl$ to fused silica slip generally increased the modulus of rupture of cast and fired (>2-1/4 hr at 2200 F) specimens by up to 40 percent, or to a value as high as 7500 psi, according to the report from General Dynamics/Pomona. Mullite formation was not observed, nor was the cristobalite content of fired specimens affected by the addition; thus, improvement in strength could not be rationalized in terms of these more likely phenomena. It was also observed in companion studies that slips containing greater amounts of impurities (Al_2O_3, MgO, CaO) fired to higher strength specimens (6000-psi modulus of rupture) than did the high-purity Glassrock slip (4800-psi modulus of rupture).

Mixtures

Investigation of thermal and thermomechanical behavior of metal-infiltrated, honeycomb-reinforced porous refractory carbides was continued (see Summary of the Ninth Meeting of the Refractory Composites Working Group Meeting) at Avco. Tantalum monocarbide, 62 and 75 percent dense, and CbC were infiltrated with Cu-10Ni alloy (TaC), lead (TaC), and copper (CbC). Composite specimens were tested in Avco's hyperthermal plasma facility with a cold-wall heat flux of 1400-1500 Btu/ft^2-sec. Spalling of the carbide skeleton varied according to the infiltrant used:

Matrix	Infiltrant	Time in Plasma to Start of Visible Spalling, sec
TaC	None	0
TaC	Cu-10Ni	13
.aC	Pb	7
CbC	Cu	6

Frontal temperatures ranged from 4830 to 5100 F in these tests. The backface (3/4 inch removed from the hot face) temperature lag was substantially greater for the carbide (open or infiltrated) than for copper-infiltrated tungsten used as reference. In 30-second tests, surface recessions were as follows for the various composites:

Matrix	Infiltrant	Surface Recession in 30 Seconds, mils
TaC	Cu-10Ni	110
TaC	Pb	80
CbC	Cu	160

Avco predicts that composites such as these may soon find application in hyperthermal environments.

Development of felted ceramics was continued (see Summary of the Ninth Meeting of the Refractory Composites Working Group) at Georgia Tech's Engineering Experiment Station. Furnace limitations resulted in problems that caused temporary deferment of studies of wood-fiber-felted ceramics. Kaowool (alumina-silica fiber) felts, impregnated with alumina, have been prepared and fired. The resulting porous ceramic boards were infiltrated to give a transpiration-cooling component of hydrated silica. Oxyacetylene testing of specimens to evaluate their thermal response is in progress.

General Dynamics/Fort Worth reported on their continued evaluation of ablative bodies for protecting reentry vehicles. Preliminary results indicate "an advantage of using low-density corks and silicones in the afterbody section of a hypersonic flight or entry vehicle when shear forces are low and the major cooling medium desired is insulation rather than ablation". Also indicated was an "advantage of filament reinforcement in the char layer in a high-shear area. For leading-edge or nose-cone application, the order of performance was composites, corks, and silicones. The char provided by the low-density corks and silicones will not withstand the shear forces imposed at the high stagnation points of reentry vehicles. Consequently, the system erodes before its complete function is performed. The composite materials provide a comparatively good char, and provided cooling by

ablation, reradiation, transpiration, and insulation media."

Continuation of studies on the preparation and evaluation of macrolaminate particle composites at Boeing is being sponsored by the Bureau of Naval Weapons and Army Transportation Research. Under Navy sponsorship, determinations of the effects of variations in macrolaminate particle size, distribution, and shape, cold and hot pressing, and sintering on the flexural strength, density, oxidation behavior, and compressive ductility of the $(HfO_2$-$5CeO_2)$-2MgO-Mo system are being studied. Preliminary results were described in qualitative fashion by Boeing. Flexural strengths from about 36,000 to 58,000 psi (at room temperature?) were obtained, depending on preparation method. It was stated that "much additional work is needed to bring this composite composition under complete control". In the Army program at Boeing, MgO-Ni-base macrolaminates are being developed to provide greater oxidation resistance than macrolaminates containing molybdenum. In this system, the strengths of the components appear synergistic; additional chemical modifications are being studied to further improve the composite strength. Currently, the $(MgO$-$5HfO_2)$-$(Ni$-$0.2ThO_2)$-0.2TiN system is being studied. (TiN improves the MgO-Ni interfacial bond.) Flexural yield strengths in excess of 50,000 psi were cited in this system. Other materials of interest are macrolaminates composed in the (Ni-Cr)-Al_2O_3 system. Weight gains of less than 4 mg/cm^2 in 100 hours at 2300 F in air, and flexural yield strengths of greater than 60,000 psi were mentioned by Boeing. Hot-strength evaluation of the (Ni-Cr)-Al_2O_3 composite is planned.

An Air Force-sponsored program at IIT Research Institute (IITRI) is evaluating selected mechanical and physical properties of commercial refractory composite structural materials. JTA graphite (48 percent carbon, 35 percent zirconium, 8 percent boron, 9 percent silicon) has been tested to determine:

(1) Flexural strength versus temperature (to 4000 F)
(2) Modulus of elasticity versus temperature (to 4000 F)
(3) Creep behavior in flexure (3180 and 3630 F)
(4) Thermal conductivity (to 3600 F)
(5) Enthalpy (to 3600 F)
(6) Specific heat (to 3600 F).

Anisotropy was considered in these evaluations. The complexity of the data preclude their review in this summary. The tensile strength and elastic modulus of Boride Z (81.1% ZrC, 13% $MoSi_2$, 5.9% BC) were also reported.

The ductility of Cr-2MgO and Cr-6MgO-0.5Ti (Chrome 30), produced by Bendix, was evaluated by Pratt & Whitney. Good tensile ductility of Cr-2MgO at 300 F was lost at room temperature, whereas Chrome 30 retained substantial tensile ductility at room temperature. Chrome 30 was completely embrittled at room temperature by nitrogen contamination resulting from a 100 hr, 2000 F oxidation exposure. The Cr-2MgO exhibited pronounced notch sensitivity at room temperature with a notch acuity (K_t) of 4.6; Chrome 30 was much less notch sensitive. The ductile-to-brittle transition under impact loading was probably about 500 F for Chrome 30 and even higher for the Cr-2MgO material.

Coated-Refractory Systems

Metallic Substrates

Coating and Process Development. A report from Sylcor reviewed three Air Force-sponsored programs dealing with the development of coatings for refractory metals. In the first-described program, several of the more popular coating-substrate combinations are being investigated. During diffusion reaction to form protective intermetallic coatings, proportionate reaction between coating and substrate has been found to be the rule. An exception occurs with the B-66 columbium alloy (containing 5 percent vanadium) substrate. In this case, vanadium is particularly concentrated in the subsilicide layer. By control of coating chemistry, oxide species may be favorably altered. For example, modification of the usual $CbSi_2$-type coatings for columbium with titanium or chromium can suppress the detrimental formation of Cb_2O_5 at elevated temperatures, according to the Sylcor findings. The second program discussed involves development of fused slurry coatings of the silicide type. In addition to standard cyclic oxidation testing, slow-cycle oxidation, stepdown oxidation testing, and reduced-pressure testing are included in the evaluation program. For columbium alloys (D-43), coatings based on a Si-20Cr-5Ti slurry composition appear most promising. Coated 10-mil-thick D-43 sheet specimens retained excellent tensile properties at room temperature and 2500 F, even after an 8 hr, 2500 F oxidation exposure (i.e., converse to the adverse effects noted by Solar and described later in this summary, for a titanium-rich coating on D-43). For tantalum alloys (T-111), coatings based on a Si-20Ti-10Mo composition appear most attractive, and for Mo-TZM, a Si-45Fe slurry appears attractive based on limited studies to date. An interesting facet of this work is the possibility for brazing and coating in one operation using the fused-slurry method. The third program described concerned the scale-up of the Sn-Al-(Mo) slurry coating process for tantalum alloys. The application of coatings to Ta-10W leading edges for Martin and corrugated heat-shield panels for NASA-Langley were discussed. Coating repair methods also were mentioned.

Research and development efforts at Marquardt on Hf-Ta alloys for high-temperature protective coatings for refractory metals were summarized. The optimum binary composition for achieving minimum combined external scale and internal reaction zone thicknesses was defined as Hf-27Ta. Because the reaction zone thickness is controlled at least in part by the facility of stabilizing the α-Hf phase by oxygen, more effective β-phase (bcc) stabilizers than tantalum should improve overall oxidation behavior by providing effective restriction of reactive zone thickness at lower alloying levels (hence, with a decrease in thickness of the outer oxide) than is the case with the Hf-27Ta alloy. Tests of a Hf-19Ta-2.5Mo alloy indicate even stronger effects than expected as qualitatively indicated below:

Alloy	Oxidation Rank(a) Relative to Oxide Thickness	Reaction Zone Thickness
Hf-19Ta-2.5Mo	A	A
Hf-20Ta	C	D
Hf-27Ta	D	B

(a) A>B>C>D in desirability.

Hot-pressure-bonding trials (2200 F, 1 hr, 2000 psi) showed the Hf-27Ta alloy to bond readily to Ta-10W, T-111, TZM, D-36, Cb-752, and tungsten. Plasma-spray-coating and hot-roll-cladding procedures are currently under development at Marquardt with the cooperation of Wah Chang Corporation. The tensile properties of Hf-27Ta were briefly studied; data are summarized in Figure 1. Specimens were fabricated from as-rolled, 30-mil-thick sheet. Tests were conducted in argon after holding for 5 minutes at temperature. Strain rates of 0.001/0.01 sec^{-1} to yielding-rupture were used.

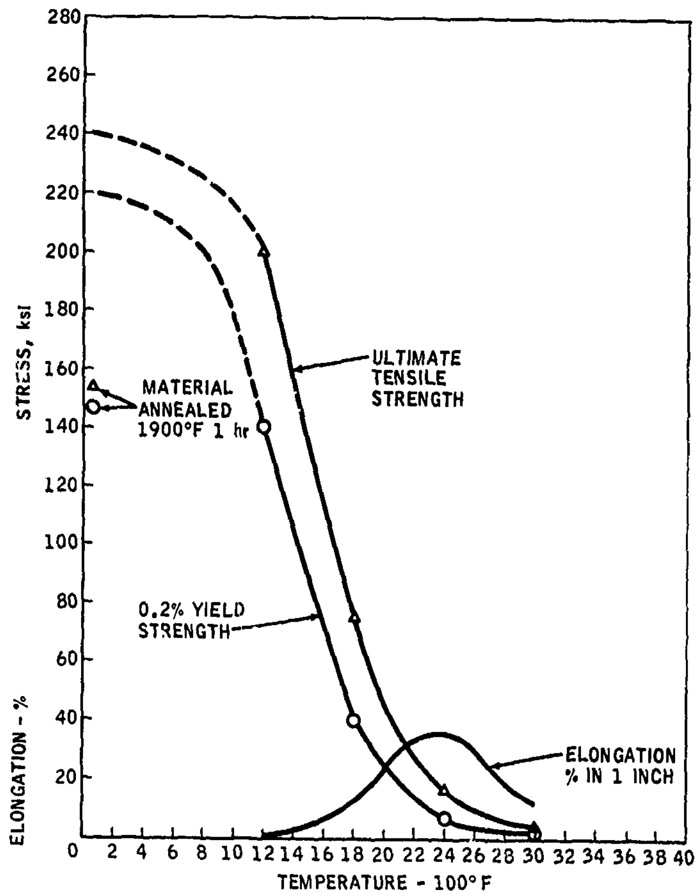

FIGURE 1. TENSILE PROPERTIES OF Hf-27Ta ALLOY (Courtesy of the Marquardt Corporation)

The kinetics of oxidation of Hf-(20/25)Ta-base alloys for use as protective coatings for tantalum at high temperatures (>3500 F) received attention at IITRI. In general, the alloys tended toward parabolic behavior in 30-minute oxy-hydrogen torch tests at a temperature near 3650 F (uncorrected optical temperature was 3500 F). However, the possibility of linear oxidation in more than one mode could not be discredited. Several postulates regarding oxidation mechanisms were discussed. Studies of the oxidation behavior of iridium-base alloys containing hafnium and tantalum were also continued. The most recent data are summarized in Figure 2. The Ir-10Ta-10Hf alloy appears the most stable of these; this was also indicated by metallographic observations.

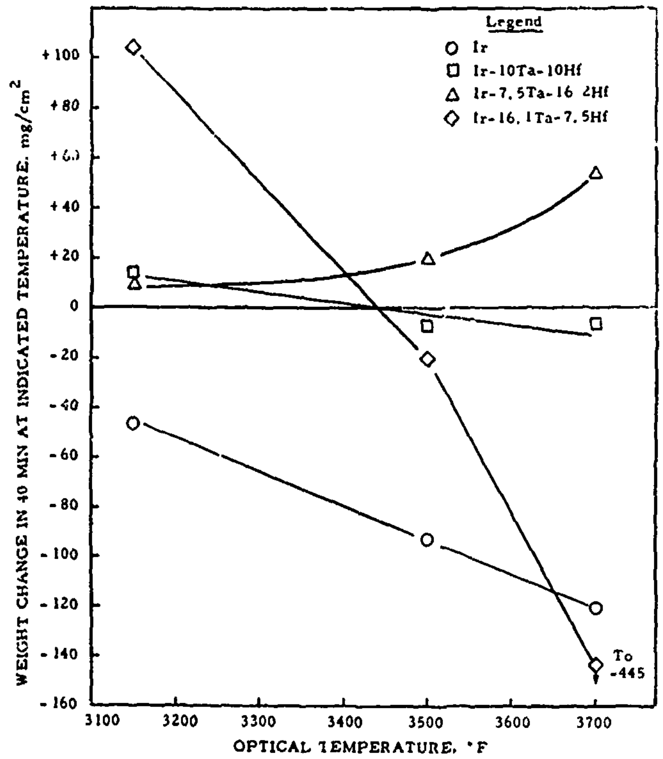

FIGURE 2. OXIDATION BEHAVIOR OF Ir-BASE ALLOYS IN AN OXYGEN-HYDROGEN TORCH FLAME (40-MIN EXPOSURES) (Courtesy of IIT Research Institute)

Continued studies of growth rates of several rare-earth sesquioxides and complex refractory oxides as potential high-temperature coatings for tungsten were described by GT&E workers (see Summary of the Ninth Meeting of the Refractory Composites Working Group). By preparing dilute alloys of rare earths in gold, parabolic growth of most of the rare-earth sesquioxides was achieved during oxidation at 2550 to 2910 F. The rate constants were too large to suggest utility at the target temperatures for the protection of tungsten (e.g., >3600 F). However, a marked decrease in oxide growth rates with increasing atomic number of lanthanide series elements (see Figure 3) warrants further investigation of elements more advanced in this series. Improved techniques for preparing diffusion couples for evaluating growth rates of complex oxides were described. Ensuing studies of $CaHfO_3$, $CaCr_2O_4$, $MgCr_2O_4$, and Ce-Cr-O and Y-Al-O oxides indicated marginal utility for only $MgCr_2O_4$, although its rate of diffusion-controlled formation at 3450 F was about one order of magnitude greater than the desired rate at 3630 F.

McDonnell reviewed the technology of slurry coatings (LB-2, L-7, TS-137—see page 5 of the Summary of the Ninth Meeting of the Refractory Composites Working Group) for refractory metals. For the LB-2 coating for columbium alloys (initially developed under the MAC-GE-AF "Hot Structures" program), evolution of processing steps has resulted in the following:

(1) Elimination of ball milling has simplified the process for slurry preparation.

(2) Acetone has been replaced by xylene, resulting in a more stable slurry.

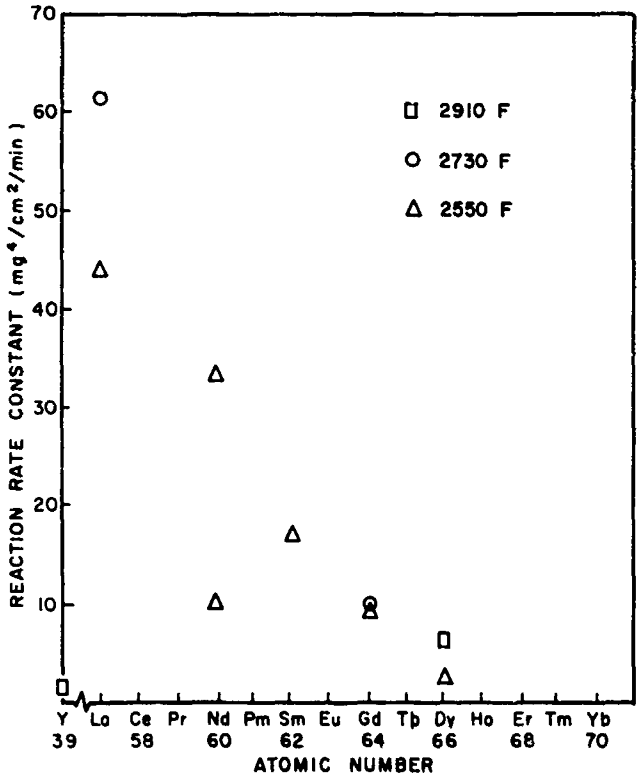

FIGURE 3. PARABOLIC REACTION-RATE CONSTANTS FOR OXIDATION OF THE RARE-EARTH METALS (Courtesy of General Telephone and Electronics Laboratories, Inc.)

(3) A postdiffusion pickle in 1:1 HCl acid is employed to remove residual free aluminum and slurry "crust", providing a smooth coating surface (this does not attack the intermetallic coating).

Typical parameters for LB-2 coating thickness as a function of slurry thickness, diffusion temperature, and diffusion time at temperature for the usual MAC furnace retort heating rate of 700 F/hr are shown in Figure 4. Processing for L-7 (for molybdenum) and TS-137 (for columbium alloys) coatings was described in some detail. The TS-137 is a 2-cycle slurry coating. The L-7 coating is now considered a production coating by McDonnell and is currently being used in numerous programs. Its "95 percent probability" life of 16 hours at 2600 F determined by the University of Dayton compared favorably with most of the other commercial coatings on TZM.

The development of electrophoretically applied coatings to protect tantalum alloys from oxidation was described by Vitro. Intermetallic coatings have been prepared on the T-222 alloy by two techniques:

(1) Thermal diffusion of electrophoretic layered coatings of the W-Si and Mo-W-Si types

(2) Sintering of WSi_2 layers applied electrophoretically.

Static oxidation lives of specimens evaluated to date range from 12 to 870 minutes at 2700 F and from 12 to 420 minutes at 3000 F. These preliminary results indicate the necessity for substantial improvement in reliability. Gradated coatings have

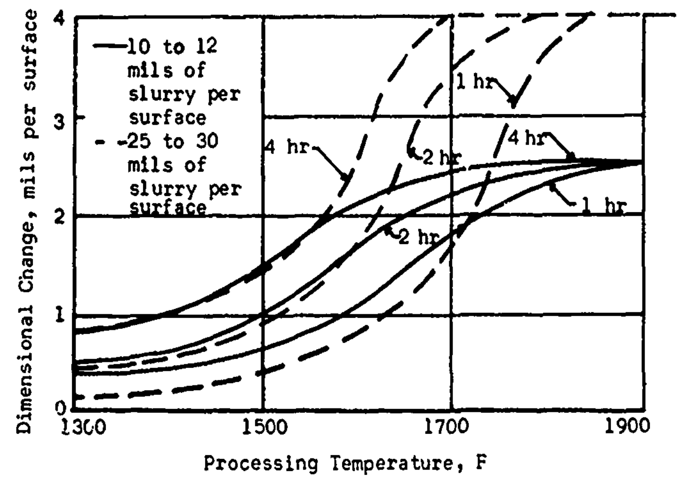

FIGURE 4. DIMENSIONAL CHANGE OF SUBSTRATE UPON APPLICATION OF LB-2 COATING AS A FUNCTION OF PROCESSING TEMPERATURE (Courtesy of McDonnell Aircraft Corporation)

been applied to Ta-10W alloy by the pumping system described at the Ninth Meeting of the Refractory Composites Working Group. These consist of intermetallic inner layers gradated to oxidic outer layers in the following systems:

Ta-10W:$MoSi_2$ $\xrightarrow{gr}$ ZrO_2(CaO stabilized)

Ta-10W:WSi_2 $\xrightarrow{gr}$ $CaZrO_3$.

Test results for these coatings were not cited.

Boeing described the behavior of the TiC-emittance-improvement topcoat for disilicide-coated TZM. Under typical reentry conditions (X-20 vehicle) this topcoat improved emittance. It is unaffected by weathering, and adhesion is good under bending and vibrational conditions. In a current Air Force-sponsored program, Boeing will develop procedures for applying vanadium-modified disilicide coatings to C-129Y columbium alloy and Ta-10W, and a Cr-Ti-Si coating to Cb-752 and FS-85 columbium alloys, using the fluidized-bed process. A brief supplementary report from Boeing reviewed the broad scope of development and evaluation activities in the area of coated refractory metals for the radiatively cooled X-20 reentry vehicle, and referenced documentation of various subjects in this area. This commentary emphasized the necessity to tailor material and evaluation parameters for the intended application, and concluded that as a result of intensive activity on the X-20 program, "the capability to manufacture quality components of coated refractory alloys was established. However, the full potential...has not... been achieved".

The chemical vapor deposition process for siliconizing tantalum by hydrogen reduction of $SiCl_4$ was described in an American-Standard presentation. The introduction of gaseous hydrocarbons to the siliconizing system produced a coating consisting of of $TaSi_2$ and TaC mixed phases. This result was determined by X-ray analysis, but was not apparent in routine metallographic observations.

Brief resumes of two completed programs, sponsored by the Air Force, concerned with (1) scale-up of the pack-cementation process, and (2)

determining practically of other methods for coating refractory metals, were presented by Pfaudler. The following pertinent comments relative to status and future development requirements were offered:

(1) Pack-cementation processes are highly developed; "the long time required to heat the retort center makes necessary the limitation of one retort dimension to a value somewhat smaller than 3.5 feet".

(2) Fluidized-bed techniques are highly versatile, but require high initial capital investment. "The area of chemical composition still needs further development...to utilize the great versatility".

(3) Slurry techniques are versatile and economically attractive. "The main problem area is not in application, but in performance...Further development is needed in coating chemistry".

(4) Fused-salt processes are feasible, but "much more laboratory work is required, both on the chemistry of salt baths and on the equipment utilized".

Variations in chemical vapor deposition processes for applying protective coatings to refractory metals (B-66, D-43, and TZM are the model substrates) are being developed at Vought Aeronautics under Air Force sponsorship. Solid coating materials characteristic of pack-cementation processes were applied as slips; Glyptol and phosphoric acid were defined as adequate binders. Heating the slip-coated substrates in (1) an inert, particulate-solid pack, (2) molten salt, or (3) open gas environment was studied. In general, the best coating results were achieved in the gaseous heating environment. Activator source has been (1) integral in the slip, (2) segregated (solid salts) from the slip or pack mix in the processing retort, or (3) by streaming a halogen gas that is produced externally. Exothermic heating has been studied; the most compatible exothermic media is a powdered mixture of 30 parts titanium, 40 parts CrO_3, and 30 parts Al_2O_3. Upon ignition, controlled temperatures between 2400 and 3000 F are maintainable for 3 to 5 minutes. This method may be used for general coating application or for repair in the field. Coating lives accruing from the various process modifications approach those of conventional pack-cementation coatings, but are not quite so good.

By judiciously controlling the activities of substrate and coating materials in the pack-cementation process, Lockheed researchers hope to improve the chemical control, vary coating composition at will, and hence improve performance of coated-refractory-metal systems. For example, the coating deposited on tantalum from a pack mix containing particulate $TaSi_2$ instead of elemental silicon, in addition to a halide salt and inert filler, was the Ta_5Si_3 compound. Previously applied $TaSi_2$ coatings on tantalum have been modified with aluminum by pack cementation using $TaAl_3$ as a coating (modifier) source material and NaCl as the activating salt. Oxidation data on modified coatings are not yet available.

Properties of Coated Systems. Lockheed's current Air Force-sponsored program to characterize the low-pressure, high-temperature behavior of commercial coated-refractory-metal systems was reviewed. The systems being studied are TZM/PFR-6, TZM/Durak B, TZM/Disil, Cb-752/Cr-Ti-Si, Cb-752/PFR-32, B-66/Cr-Ti-Si, and Ta-10W/Sn-Al (the Cr-Ti-Si coatings were applied by TRW). In addition to static-environment base-line data, the effects of gas velocity, temperature and pressure cycling, gas dissociation, vacuum exposures, and intentional defects will be evaluated. Preliminary qualitative results of testing in Mach 3 air flow indicate the liquid-phase-reliant Sn-Al coating is severely degraded relative to its static behavior, that all TZM-based systems are somewhat degraded, and (implied) that Cb-base systems are only slightly affected by the dynamic environment. The importance of subcoating diffusion zones (typically M_5Si_3 phases) to good coating performance was cited by the Lockheed report.

Honeycomb panels of D-43 columbium alloy protected by the TRW Cr-Ti-Si coating displayed nonuniform coatings and premature failures in oxidation tests at Martin. This difficulty was traced to inadequate temperature control during coating of the large panels (15 by 38 inches). The Martin report referred to the crack-arresting behavior of the $CbCr_2$ phase of the coating. Martin also determined the tensile properties of Sn-Al-coated T-111 (recrystallized) tantalum alloy, from which leading edges have been formed. At temperatures through 1800 F, tensile properties of the coated T-111 were comparable to those of uncoated material. At 2200 F, however, yield and tensile strengths fell precipitously and were somewhat less than normally possessed by the uncoated alloy at 2700 F, for example. This unexpected behavior was not explained.

The response of LB-2-coated Cb-752 to low-pressure isothermal environments (essentially static, controlled-leak tests) is being studied by McDonnell. Weight-change data for exposures up to 3 hours at pressures from 0.01 to 10 torr and temperatures from 1300 to 2900 F were reported. At 1 and 10 torr, continuous weight gains were observed at all temperatures, and at 0.01 torr, continuous weight losses were observed. At 0.1 torr, abnormal thermal and kinetic effects on weight change were noted. Reasons for these effects are expected to be elucidated by continuing research.

The suitability of Sn-Al coated Ta-10W for heat-shield applications is being investigated at NASA-Langley. Initial evaluations were conducted on sheet coupons, small single-skin corrugated sandwiches, and small leading-edge shapes, all fabricated from 5- to 8-mil-thick Ta-10W. Continuous and cyclic furnace and dynamic arc-jet (subsonic) oxidation tests were performed. Test results are summarized in Table 2. Pertinent observations are that (1) thermal cycling reduces coating life, (2) life of the system is shorter for the more complex sandwich shape than for simple coupons at higher temperatures, (3) a dynamic environment drastically reduces protectivity of the Sn-Al coating, and (4) ignition occurred at temperatures as low as 2600 F. (Previously reported ignition temperatures for uncoated tantalum alloys are in excess of 3000 F, suggesting the possibility

TABLE 2. RESULTS OF OXIDATION TESTS ON Ta-10W FEASIBILITY SPECIMENS COATED WITH Sn-27Al-5.5Mo COATING

(NASA-Langley; tested in air at atmospheric pressure except as noted.)

Specimen	Test Apparatus	Test Conditions	Test Temperature, F	Time to Failure, hours	Substrate-Thickness Loss, in.(a)
Coupon	Furnace	Continuous	2300	>230(b)	0.0041
			2600	>190(b)	0.0035
			2600	>5(b)	0.0017
			2600	>20(b)	0.0019
			2900	>75(b)	0.0031
		1-hour cyclic	2000	45	0.0009
			2300	18	0.0022
			2600	10	0.0026
			2900	10	0.0025
			2900	6	0.0019
		1-hour cyclic(c)	2400	>20(b)	0.0026
Sandwich	Furnace	1-hour cyclic	2300	>10(b)	
			2600	>10(b)	
			2750	3	
			2900	1.2	
Leading edge	Arc jet	0.1-hour cyclic	2300	>1(b)	
			2600	0.50(d)	
				0.58(e)	
			2900	0.20(d)	
				0.25(e)	

(a) Based on as-coated substrate thickness of 0.0074.
(b) Tests discontinued for metallurgical examination.
(c) Tested at 0.5 mm Hg.
(d) First visible failure.
(e) Ignition.

of catastrophic coating-substrate-environment interaction in this system.) Larger, 10 by 18-inch heat shields have been fabricated and are scheduled for evaluation.

Solar reported activities concerning the investigation of (Cr-Ti)-Si-coated columbium alloys. A susceptibility of the TRW coating to failure in fairly short times under conditions involving slow thermal cycling (stressed at 2 to 3 ksi) between 800 and 2500 F (mean cooling rate of ~60 F/min) was described. It was further shown that the TRW coating applied to D-43 alloy foil seriously degrades the substrate strength; this did not occur with Cb-752 or B-66 substrates. This effect was ascribed by Solar to gettering of carbon from the D-43 substrate by the titanium-bearing coating. In another program, Solar investigated the oxidation behavior and thermal-expansion coefficients of a number of bulk disilicide and nominal M_5Si_3 materials prepared by melt homogenization, crushing, and powder-metallurgy consolidation. Of principal importance was that the Ti-Cr-Si system possesses unique tolerance for columbium, and that the M_5Si_3 compounds in this system display excellent oxidation behavior, appearing at least as good as the MSi_2 compounds in this respect. The potential thermal-expansion-mismatch-induced stress mitigation of the M_5Si_3 phase was acknowledged.

Attractive features of two newly developed aluminum-base coatings for superalloys were described by Chromalloy. When applied over B-1900 superalloy, these coatings, called OT and MOT by Chromalloy, provided up to at least 180 hours' protection in a hot-gas erosion test with very little weight change, compared with less than 100 hours for a comparative commercial coating. In addition, the new coatings have about a 50 F advantage over most prior coatings regarding melting point, are relatively soft (~500 VHN), and resist impact failure to a much greater extent than other coatings, according to Chromalloy.

Marquardt's vapor-deposited SiC has been briefly evaluated as a high-temperature protective coating applied to various refractory substrates. Table 3 presents the results of torch testing of specimens at temperatures above 3000 F.

TABLE 3. MARQUARDT RM-005 (SiC) COATING-PERFORMANCE OXYACETYLENE-TORCH-TEST SUMMARY

Substrate	Coating Thickness, in.	Temperature, F	Time	Remarks
Tungsten, 1/2 x 6 x 0.040" strip	Uncoated	3400	2 min	Complete burn-through
	0.020	3200	>4 hr	No failure, test terminated
	0.034	3400	>7 hr	No failure, test terminated
	0.023	3600	1 hr	Bottom edge failure
Tantalum-10W 1/2 x 6 x 0.040" strip	Uncoated	3250	<2 min	Complete burn-through
	0.010	3600	36 min	Cracked during thermal cycle
Molybdenum, 2" dia x 3" high cylinder, 0.060"-thick wall	Uncoated	3000	2 min	Complete burn-through
	0.006	3100	2 hr	No failure, test terminated
Graphite, 1/2 x 1 x 4" bar	Uncoated	3000	10 min	Complete burn-through
	0.020	3200	4 hr	No failure, test terminated
	0.020	3400	4 hr	No failure, test terminated
	0.020	3600	1 hr	No failure, test terminated

The shear strength of alumina coatings sprayed on steel was determined at NASA-Lewis. The coatings were plasma sprayed under conditions to maintain a substrate temperature of about 330 F within 40 mils of the coating-substrate interface; purely mechanical bonds resulted. Figure 5 illustrates the test results. To provide various degrees of roughness of the steel to which coatings were applied, the steel test area was grit blasted under controlled conditions. Bond shear strength increased with increasing roughness of the substrate. The fixture in which coatings were applied and tested is shown in Figure 6.

Coated Graphite

Having defined iridium as being a particularly attractive potential coating material for graphite based on its low permeability by oxygen (see Summary of the Ninth Meeting of the Refractory Composites Working Group, page 8), researchers at UCC Carbon Products conducted studies on the compatibility between graphite and iridium and investigated several methods for applying iridium coatings. Eutectic melting between iridium and carbon was detected at 3830 ±45 F when samples were heated for 3 hours at that temperature. The apparent eutectic temperature is sensitive to time owing to the "slow rate of carbon diffusion in iridium". Bonds formed between graphite and iridium upon heating to temperatures from 4700 to

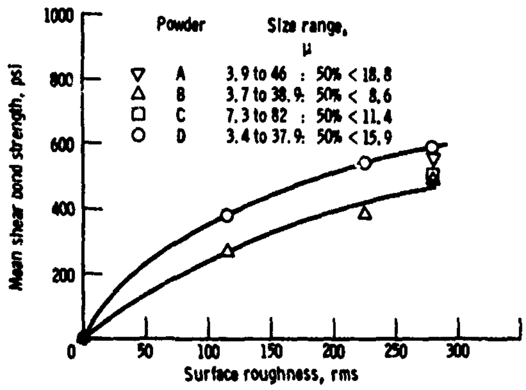

FIGURE 5. MEAN SHEAR BOND STRENGTH AS FUNCTION OF SURFACE ROUGHNESS FOR FOUR VARIETIES OF ALUMINA COATINGS ON 304 STAINLESS STEEL
(NASA-Lewis)

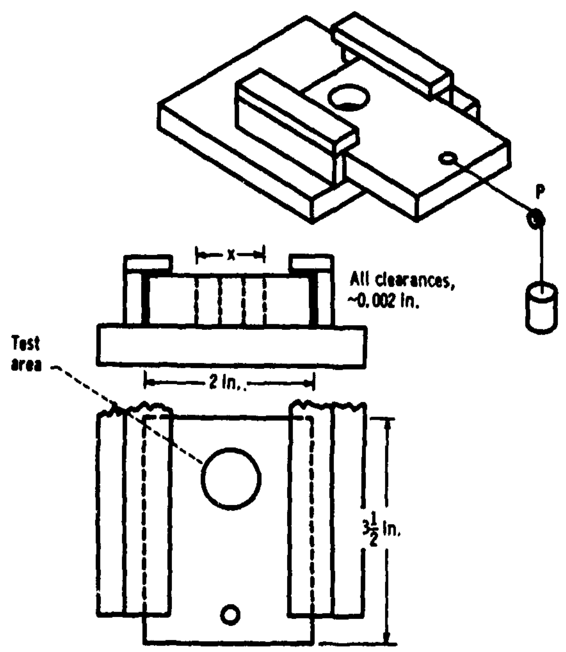

FIGURE 6. SHEAR-BOND-TEST APPARATUS
(NASA-Lewis)

5000 F are very strong; fractures occur in the graphite body. Fused slurry, foil cladding, vapor plating, and electroplating methods for applying iridium to graphite were described. The most satisfactory-appearing coatings resulted from a combination of slurry, vapor plating, and electro-deposition methods. Performance data for such coatings were not presented.

Fiber-Reinforced Composites

Metal Matrix

Fiber-reinforced nickel composites have been prepared by researchers at General Technologies Corporation using "molecular forming techniques... at ambient pressure" and at "temperatures near ambient". Composites comprising continuous uni-directional fiber reinforcement of a nickel matrix by tungsten and boron filaments, among others, have been prepared and evaluated for strength:

Reinforcement Filament Material	Vol %	Measured Ultimate Strength of Composite, psi	Composite Efficiency, %
W	3	135,000	98
W	4	154,000	110
B	24	308,000	136
B	75	384,000	134

At this time, reasons for variations in composite efficiencies are not altogether clear. Nickel composites reinforced with sapphire whiskers and with graphite cloth were prepared to demonstrate the utility of the GTC forming methods.

Researchers at Battelle-Northwest reported on the mechanical properties of nickel reinforced with tungsten wire prepared by pneumatic impaction (Dynapak). Two modes of reinforcement with 1-mil tungsten wire were studied:

(1) Continuous wires aligned in the direction of loading in tensile-test coupons

(2) Random orientation of chopped tungsten wires:

(a) 1/4 to 1/2-inch lengths
(b) 2-inch lengths.

The various powder-fiber blends were encapsulated in stainless steel, evacuated, heated to 2000 F, and impacted at 255,000 psi. Compacted densities were about 99 percent of theoretical. Tensile tests at room temperature and at 1925 F gave the following results:

Test Temperature, F	Tungsten, vol %	Distribution	0.2% Offset Yield Strength, psi	Ultimate Tensile Strength, psi
80	None	--	34,400	53,300
80	1	Random	34,800	53,600
80	10	Aligned	58,100	61,400
1925	None	--	3,100	3,450
1925	1	Aligned	4,100	4,100
1925	1	Random	3,300	3,400
1925	5	Aligned	7,000	7,400
1925	10	Aligned	19,000	19,000

Thus, effective strengthening was observed only in specimens employing the continuous aligned tungsten wires. At room temperature, the tungsten fibers fractured into short lengths with only slight strain, although the strengthening effect was maintained. The presence of the wire apparently restrained the nickel from microscopic and macro-scopic necking, and ductility was lowered, although cracks in the tungsten did not propagate into the nickel. At high temperatures, tungsten and nickel deformed homogeneously. Substantial reaction between the nickel and tungsten as a result of tensile testing at 1925 F was noted. These preliminary studies indicate promise for composites of this type.

Reinforced-metal composites comprising an aluminum-alloy matrix reinforced with steel wire have been prepared at Harvey. These composites were successfully prepared by diffusion bonding sheets of

various aluminum alloys uniformly interspersed with 9-mil 355 stainless steel wire. Alloying at the aluminum-steel interface is undesirable and does not normally occur. Some composite properties were determined at room temperature:

Property	Target	25 vol % Steel Composite	50 vol % Steel Composite
Ultimate Tensile Strength, ksi	175	172 to 176	285
Density, lb/cu in.	0.144	0.145	0.195
Strength/Density Ratio, in. x 10^{-6}	--	1.21	1.46
Elastic Modulus, psi x 10^{-6}	--	15	20

These composites have been prepared in thicknesses from 0.040 inch to 0.75 inch. The largest piece produced to date was 12 x 24 x 0.250 inch. . Similar aluminum composites reinforced with beryllium wire have been successfully prepared; material containing 25 volume percent of 10-mil-diameter beryllium wire exhibited a tensile strength of 100,000 psi, modulus of 17.5 x 10^6 psi, and density of 0.09 lb/cu in.

Oxide Matrix

Studies of Allison involved determination of elastic modulus, modulus of rupture, thermal shock, and oxidation behavior of hot-pressed mullite reinforced with 20 volume percent of about 60-mil lengths of 20-mil-diameter tungsten or molybdenum wire. The measured modulus of rupture for the composites was 30 to 50 percent greater than expected based on elastic theory of matrix reinforcement. Average measured rupture strengths ranged from about 20,000 to 24,000 psi at room temperature, compared with an expected value of about 15,000 psi. Although the formation of microcracks in the mullite matrix could account for the greater-than-expected strengthening, no physical evidence of microcracks was found. Elastic modulus and thermal-shock resistance of the composite specimens were considerably improved over properties for monolithic mullite. Oxidation behavior of the composites, however, was so poor as to preclude the use of this material for long-time service as, for example, in gas-turbine components. Siliconizing of the refractory-metal fibers did not improve oxidation behavior to the extent desired.

A composite consisting of petalite ($LiO_2 \cdot Al_2O_3 \cdot 8SiO_2$, thermal expansion coefficient of 0.11 x 10^{-6}/F) containing 20 volume percent of 1/8-inch-long by 2-mil-diameter molybdenum wire was blended and hot pressed at 2410 F and 3000 psi at IIT Research Institute. Based on thermal-expansion coefficients and elastic modulus of the constituent phases, the compressive prestress calculated for the ceramic matrix was 7,300 psi. Whereas the unreinforced ceramic exhibited a modulus of rupture of 12,200 psi, that of the reinforced composite was 19,400 psi, in very good agreement with calculations.

Additional studies of the mechanical behavior of continuous-wound, filament-reinforced, slip-cast fused silica (see Summary of the Ninth Meeting of the Refractory Composites Working Group) were reported by Georgia Tech. The axial compressive strength of 3/4-inch-diameter cylindrical fused-silica specimens was increased two to three times by winding with two or four layers of 16-mil fiber-glass yarn under tension (4-1/2 or 8 lb). The transverse strength (MOR), normal to the filament winding axis, was not significantly improved by filament winding, although the resin binder used to secure the wound filament effected 80 percent increase in transverse strength. When a two-dimensional glass cloth was placed between the fused-silica specimen and the filament winding, transverse strength showed 250 percent increase, and axial compressive strength characteristic of the simple filament-wound specimens was almost completely retained. Hoop strength of wound filament-reinforced fused-silica rings was determined in appropriate test adaptors. The hoop strength of the silica component (first crack) was from five to nine times the value of an unreinforced body, and the overall composites strength (catastrophic failure of the composite system) was as much as 25 times the strength of the bare silica ring. Two-layer, tension-wound, 3-mil-diameter steel-wire-reinforced hoop specimens were also prepared and tested. Hoop strength of the silica base compared favorably with that of the bulkier fiber-glass wound specimens, although the ultimate strength of the system was not so great. Strengths determined in this study are summarized in Table 4.

Graphite Matrix

A paper by Ling-Temco-Vought Aerospace (Astronautics) described technology of reinforced pyrolyzed plastics. Important factors governing the selection of the polymer binder to be pyrolyzed are carbon residue, pyrolyzed strength, volume and shape stability, and inertness to the reinforcement member. Cross-linked polymers appear most suitable. Aerospace has investigated systems comprising phenolics reinforced with graphite cloth, fiber-glass fabric, or woven quartz fabric. Fabrication steps include:

(1) Impregnate cloth reinforcement with plastic binder

(2) Bake out (~200 F)

(3) Assemble plies to form desired crude shape

(4) Mold to final shape (die mold, vacuum bag, or autoclave) at ~325 F

(5) Pyrolyze (carbonize) at 1300 to 1500 F for 10 to 24 hours (typical)

(6) If desired for thermal stability and strength, graphitize (~5000 F).

Numerous variations in parameters of these stages may be employed to tailor density, modulus, strength, and other properties as desired. For example, "higher strength values can be obtained on specimens molded at [higher pressures] when [followed by] the slow carbonization cycle...Since the porosity of the molded laminate provides an escape path for the decomposition gases..., the rate of decomposition must be reduced when the porosity is reduced by a density increase". Some flexural strengths cited for pyrolyzed (but not graphitized) phenolic-glass cloth and graphite-cloth composites were 9,250 psi and 3,580 psi, respective flexural modulii were 2.32 and 1.1 x 10^6 psi at room temperature. Strengths of such composites generally increase with increasing temperature up to 4000 F. Carbonized density values in

TABLE 4. MECHANICAL PROPERTIES OF PRESTRESSED SLIP-CAST FUSED SILICA (GEORGIA TECH)

Reinforcement Mode			Axial Compression Strength, ksi	Transverse Bending Strength,[b] ksi	Hoop Tensile Strength, ksi	
Material[a]	No. of Layers	Wrapping Tension, lb			Of Silica Body Only[c]	Of Overall Composite[d]
FF	2	4-1/2	46.5 (23.9)[e]	5.0 (3.0)	2.9 (0.55)	7.9
FF	2	8	48.7 (22.1)	6.9 (4.1)	3.1 (0.55)	7.3
FF	4	4-1/2	56.5 (18.1)	7.1 (3.9)	3.4 (0.55)	12.7
FF	4	8	60.3 (20.3)	6.8 (4.3)	4.7 (0.55)	13.9
FF + C	2	4-1/2	46.1 (21.9)	10.3 (2.9)	--	--
SW	2	2	--	--	3.5	5.3
Resin binder only			22.5 (20.1)	5.9 (3.3)	--	--

(a) FF = 16-mil-diameter fiber-glass filament;
C = Fiber-glass cloth, 35 threads/inch of 8-mil strand;
SW = 3-mil-diameter steel wire.
(b) Bend axis normal to filament winding axis.
(c) Indicated by first crack in silica body.
(d) Total through-failure.
(e) Parentheses indicate value of bare, slip-cast, fused-silica control specimen.

the range from 60 to about 76 lb/ft^3 were cited; thus, these composites exhibited most attractive strength/density parameters. Thermogeometric stability of graphitized specimens was excellent. Pyrolyzed composites "yield" with the application of stress beyond their ultimate strength, circumventing the purely brittle behavior characteristic of nonmetals. Thermal evaluations showed superior performance compared to charring ablators on an areal density basis. Reinforced pyrolyzed plastics appear to have excellent potential for a variety of aerospace structural and propulsion applications.

Fiber Technology

An assessment of the potential of BeO whiskers as reinforcements in composite materials was given by Atomics International. Tensile strength of a 7-mil-diameter crystal of BeO was reported as 2.7 x 10^6 psi. This compares favorably with strengths of Al_2O_3 fibers that are two orders of magnitude smaller, and, assuming the usual size-strength relationship, indicates very high strengths for BeO whiskers. Probably the most common habit of BeO whiskers orients the c-axis in the crystal-length direction, thus taking advantage of the cleavage and elastic anisotropy of BeO crystals. Figure 7 illustrates elastic anisotropy. BeO is very stable thermodynamically, refractory (although a phase change occurs at 3720 F), low density, exhibits high thermal conductivity, and has a fairly high coefficient of thermal expansion. In comparison with Al_2O_3 whiskers, BeO as a composite structural material appears most attractive.

Laboratory processes for preparing single-crystal filaments of BeO were also discussed by Atomics International. Hydrolyzation and athermal nucleation and growth of BeO whiskers, and thermal nucleation and growth from a supersaturated flux ($PbO-PbF_2$) have been explored. Of these, growth from a molten flux appears most attractive as a potential commercial process for producing continuous single-crystal filaments of BeO. Several factors involved in this process were discussed.

Norton (NRC) briefly reported on a variety of interests in the general area of fibers and thin-film technology. Potentially available from various Norton facilities are:

(1) Alumina wool--1/4 to 1 micron by 1/8 to 1/4-inch long

(2) Silica wool--1/4 to 1 micron by 1/8 to 1/4-inch long

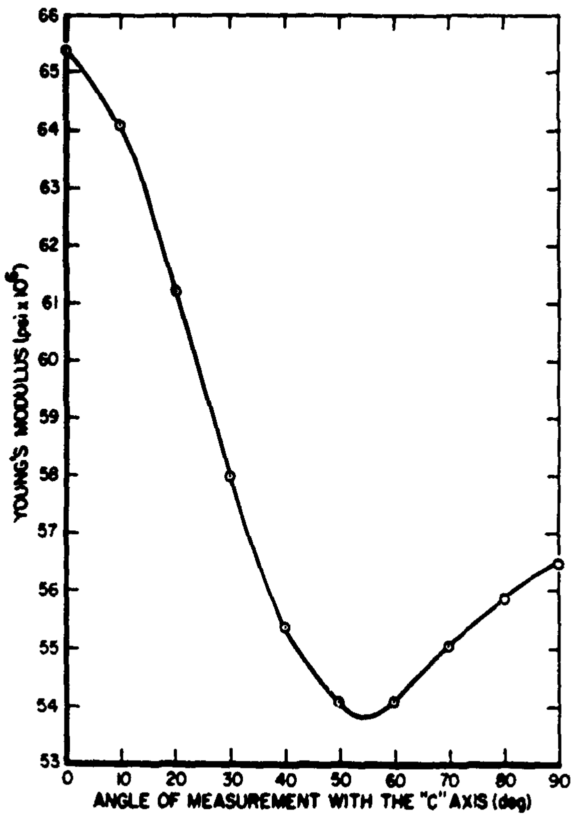

FIGURE 7. YOUNG'S MODULUS OF SINGLE-CRYSTAL BeO AT ROOM TEMPERATURE

Courtesy of Atomics International.

(3) SiC fibers--1/2 micron by 1/16 and 1/8-inch long

(4) ZrO_2 fibers (polycrystalline)-- 20 microns up to 2-inches long.

By vacuum drawing and metallizing (aluminum) prior to exposure to air, glass monofilaments retained 500,000-psi strength after residence in air for 1 week. By comparison, the strength of uncoated fibers deteriorates to 200,000 to 250,000 psi with a 1-week air exposure. Thin-film sheet, tape and flakes of tungsten, beryllium, rhenium, tantalum, and TiB_2 have been prepared experimentally. A tensile strength of 250,000 psi and elastic modulus of 50 x 10^6 psi were measured on 0.3-mil-thick tungsten film. Beryllium film exhibited a strength of greater than 100,000 psi.

Techniques for the preparation of short tungsten and tungsten monocarbide fibers for use as reinforcement members for metallic composites are under development at Narmco. Tungsten wire, undoped, 1/2 mil in diameter, is continuously strain-gradient annealed to produce linked single crystals. Samples have been carburized in 2 percent methane-98 percent hydrogen for 30 seconds at 2590 F resulting in WC crystals. The following mechanical properties have been determined at room temperature:

Material	Ultimate Tensile Strength, psi	Elastic Modulus, 10^6 psi
As-received 1/2-mil wire	617,000	56
As-received and carburized	106,000	104
Strain-gradient annealed	186,000	58
Strain-gradient annealed and carburized	Extremely fragile	

Vapor-deposited SiC (on 1/2- and 1-mil tungsten wire) filaments have been studied at Marquardt. "Additives" resulting in an "extremely fine grained...essentially amorphous" structure produced filaments with tensile strengths ranging from 184,000 to 385,000 psi (average = 289,000 psi) and an elastic modulus of 70 x 10^6 psi at room temperature. These properties were measured on 5-mil-diameter filaments with 1-inch-long test sections. When tested at 1800 F following a 1/2-hour soak in air at that temperature, filaments retained 70 to 80 percent of their room-temperature strength.

Continuous polycrystalline alumina filaments have been fabricated at IIT Research Institute by continuous extrusion-drying-firing of a paste mix. The continuous filament (20-foot lengths have been prepared) can be wound on a mandrel. For diameters of 3 mils (4-inch test length), tensile strengths as high as 70,000 psi have been obtained. Elastic modulus of 70 x 10^6 psi was measured. The strength value falls within the range of values for Al_2O_3 whiskers of this size.

Cincinnati Testing Laboratories is involved in the development of reinforced plastic composites. Platelets and whiskers of SiC are the reinforcement components for a resin matrix. Major emphasis to date has been on size and shape classification of the reinforcement particles, and obtaining desired orientations of these in the matrix. Selective adherence of 5- to 10-micron-thick SiC platelets to paper has successfully served to separate the desired species from undesired chunks, twins, and thicker platelets.

PROCESS TECHNOLOGY

The Norton Company, in conjunction with various equipment manufacturers, has developed a prototype gun for continuous Rokide spraying of oxides. A sketch of this equipment is shown in Figure 8. Special features include hopper storage for rods, positive and automatic rod feed, automatic gas valving, and quick-change air caps. The gun is water cooled and is operated completely from the central control panel. Coating application tests on actual missile components indicate a three- to fivefold increase in coating-laydown rate over current production equipment.

At Metco, a comparison between plasma-arc and oxyacetylene flame-sprayed molybdenum was made. Two flame-spraying conditions using molybdenum wire feed were employed:

(1) "Normal" deposition rates (5-8 lb/hr) at 2:1 oxygen:acetylene gas flow rates using standard 1/8-inch-diameter wire

(2) Low deposition rate (1.6 lb/hr) under more reducing conditions (3:2 oxygen:acetylene ratio) using 15-gage molybdenum wire.

The plasma was a nitrogen-hydrogen mixture and sprayed molybdenum powder at a consumption rate of 7.5 lb/hr. In all cases, molybdenum was applied to a smooth carbon steel mandrel. Table 5 summarizes Metco's findings. It was concluded that the more dense, stronger, plasma-sprayed molybdenum would probably be superior for hot applications, but the harder, flame-sprayed coatings should be superior for nonrefractory, wear-resisting applications.

Studies involving the chemical vapor deposition of tungsten plates and tubes, W-Re alloy tubes, and UO_2 were described by Oak Ridge. Problems in obtaining dimensionally uniform deposits are due primarily to variation in gas chemistry over large areas. This is controlled by providing a moving hot zone, thereby restricting the deposition area progressively. Current capabilities at ORNL allow the deposition of, for example, tungsten plates of about 100 sq in. in area, 60 to 80-mils thick, in each deposition run. Experimental details for preparing tubes of W-Re alloys (mentioned in the Oak Ridge report during the Ninth Meeting of the Refractory Composites Working Group) were discussed. Deposition conditions found satisfactory were:

Temperature:	850 to 1300 F
H_2:(WF_6 + ReF_6):	20:1
Total Pressure:	10 torr
WF_6:ReF_6 (typical):	6:1

Rhenium content varied radically but reproducibly in a uniform manner from end-to-end of the 12-in.-long tubular deposit. Research to level the rhenium content is in progress. UO_2 deposition is effected under the following conditions:

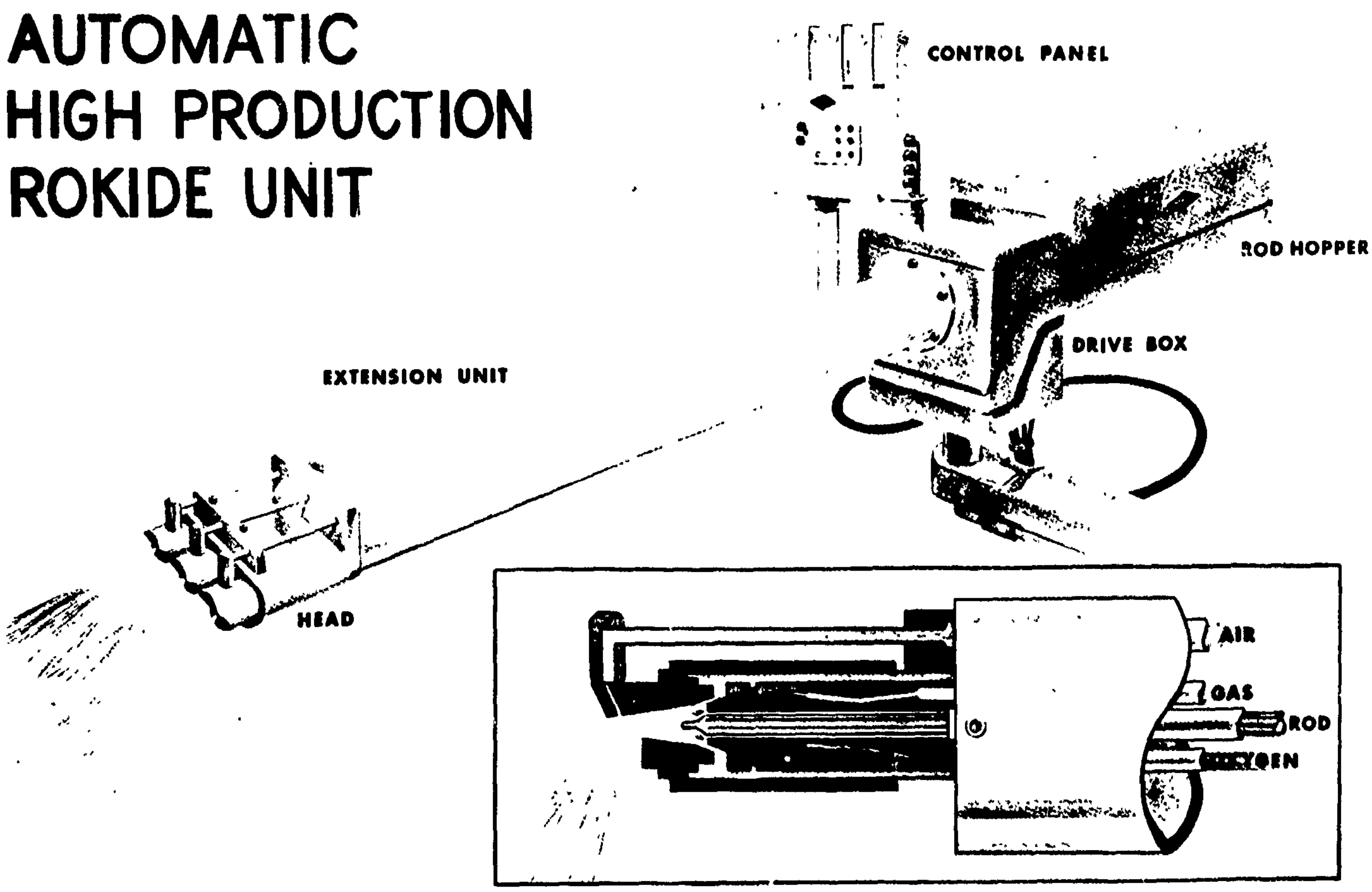

FIGURE 8. AUTOMATIC HIGH-PRODUCTION ROKIDE UNIT

Courtesy of the Norton Company.

TABLE 5. COMPARISON OF OXYACETYLENE-SPRAYED AND PLASMA-SPRAYED MOLYBDENUM (METCO)

Test	Standard Wire	15-Gage Wire	Plasma
Theoretical Density	81.5%	81.7%	87.7%
Oxide Content (MoO_2 by vol)			
Chemical	12.0%	8.5%	4.0%
Metallographic	12 ±2%	11 ±1%	4 ±1%
Percentage of voids	14.0%	15%	8.8%
Coating Hardness	R_c38-40	---	R_c25-34
Particle Microhardness	1162-1800 av 1535	---	700-1050 av 796
Self-Bonding	Yes	Yes	Yes
Tensile Strength (perpendicular to surface)	2150 psi	---	3000 psi

Temperature:	2200 to 2730 F
Total Pressure:	<10 torr
Gas Chemistry, vol %:	1 to 10 UF_6 10 to 40 O_2 60 to 80 H_2

The gases are injected into the hot zone of the reactive chamber via an appropriately designed water-cooled injector to enhance mixing under the desired conditions. Depending on process variables (within the above ranges), the UO_2 may be deposited in powder, crystalline, or dense agglomerated-shape forms. Deposition parameters outside the above ranges result in contamination of the deposits with intermediate reaction products (UF_4, UO_2F_2). UO_2 chemistry can be controlled with good reproducibility in the range from $UO_{2.001}$ to $UO_{2.166}$; fluorine contents are usually less than 50 ppm.

Defective areas in brazed columbium-alloy honeycomb sandwiches have been successfully repaired at Martin-Baltimore by (1) drilling a small hole in the skin at the location of the defective braze, (2) injecting braze-alloy powder into the internal defect area, (3) patching the hole, and (4) re-braze cycling.

To prevent bonding between silica tooling fixtures and mosaic radome structure during firing (see the summary of the Ninth Meeting of the Refractory Composites Working Group, page 10), Narmco inserted a graphite cloth parting layer, and pumped nitrogen through tooling apertures to the interface. Fabrication techniques for castable silica tooling to the precise tolerances required for the radome were described in detail. Full-size truncated-cone proof sections of the desired structure have been fabricated, and complete tooling for the final radome is currently being prepared.

SPECIFIC HARDWARE APPLICATIONS

Rocket-Motor Components

Ablative

Phenolic resins containing refractory material (silica, zirconia, alumina, graphite fibers, etc.) have been successfully used as rocket thrust chamber materials (wall and nozzle) in low-pressure (<200 psia) N_2O_4-hydrazine propellant systems. A presentation by Aeronutronic Division of Philco discussed the fundamentals involved in the use of such reinforced ablative systems. Physical and chemical interactions between ablative resin, free gas-stream products, reinforcement material, and downstream hardware were treated in considerable detail. Thermodynamic considerations may be used to predict suitable combinations of resin and its reinforcement material for given propellant chemistry, according to Aeronutronics.

Martin has fabricated resin-impregnated zirconia rocket nozzle inserts for testing at NASA. Higher density bodies (1.92 g/cc, impregnated, 1.08 g/cc ZrO_2 skeleton) than previous leading-edge and nose-cap bodies prepared and evaluated at Martin were utilized to better withstand the greater aerodynamic shear loading of this application. Test results were not available.

The manufacturing technology for chemically bonded, resin-impregnated, foamed-ceramic, ablative-insulative bodies was described by a General Technologies Corporation paper to be presented at a SAMPE meeting, which was also submitted to this Refractory Composites Working Group Meeting. The inclusion of strengthening ceramic fibers in the foamed ceramic skeleton was noted. The General Technologies paper also noted very successful hybrid motor-firing tests employing impregnated foamed ceramics for chamber insulation and mixing baffles. Firing durations up to 60 seconds' steady or 70 seconds' multiple firing, with chamber pressures up to 500 psi and high oxidizer/fuel ratio propellants producing gas temperatures of 7000 to 8000 F were employed. Some insulations have been reused as many as four times, with no indication of spalling or thermal-shock failure.

Radiative

Test results on "wire-wound tungsten nozzles" were presented by United Technology Center researchers. A variety of solid and hybrid propellants were used in these small-scale tests (1.2-in. throat diameter, maximum); temperatures from 5700 to 6800 F and chamber pressures from 315 to 2800 psia were included. Multiple start capabilities and total run times, as long as 200 seconds, have been evaluated. With extremely corrosive propellants, considerable corrosion of the throat was noted, but under more moderate conditions, the nozzles performed very well. The "high degree of performance capability" and low cost of fabrication for wire-wound tungsten nozzles is most attractive according to United Technology Corporation, and a 5-in.-throat-diameter nozzle is being fabricated to evaluate scale-up potential.

Model firing tests to evaluate various rocket nozzle insert materials were described by TRW-Equipment Laboratories. Chamber pressure of 150 psi was achieved with 50% N_2H_2 + 50% UDMH fuel and N_2O_4 at an oxidizer-to-fuel ratio of 1.62. The firing sequence included long, intermediate, and short pulsing modes typical of some attitude-control engines. Of numerous insert materials evaluated, (Si-W)-coated tungsten or molybdenum exhibited the best performance. When the combustion chamber liner contained silica, even these best materials guttered because of reaction with ejected SiO_2. Oxides (BeO and metal-modified ZrO_2) and titanium boronitride suffered from thermal shock. The erosion of JTA graphite was quite extensive.

Graphite nozzles were coated with vapor-deposited SiC by Marquardt and tested in various facilities. The results (Table 6) showed a stable system with little or no erosion.

A program to develop a model for mathematically predicting residual stresses in composite rocket nozzles arising from differential thermal expansion is in progress at IIT Research Institute. Preliminary measurement of residual stresses in rings cut from different axial locations of plasma-sprayed, gradated hafnia-coated tungsten nozzle shapes have been made. The levels of stress in the different layers vary according to axial location. The data have yet to be rationalized in terms of a mathematical model.

TABLE 6. LIQUID FUEL ROCKET TESTS USING SILICON CARBIDE-COATED GRAPHITE NOZZLES (MARQUARDT)

Test Rocket	Propellants	Approximate Test Conditions: Gas Temp, F	Pressure, psia	No. of Runs	Time	Remarks
25-lb thrust pulse rocket	N_2O_4/50-50 UDMH-N_2H_2	5000	100	1	7-min pulsing, 10-min steady state	No measurable erosion
1750-lb thrust rocket	N_2O_4/50-50 UDMH-N_2H_2	5000	150	11	40-430 sec pulsing and continuous	No erosion
100-lb thrust rocket	N_2O_4/50-50 UDMH-N_2H_2	5000	100-160	4	240-620 sec pulsing and continuous	No erosion
NASA-Lewis research rocket, 200-lb thrust	H_2-O_2	5200	100	1	679 sec	Erosion 0.0006 inch/min for 400 sec
NASA-Lewis research rocket, 200-lb thrust	N_2O_4/50-50 UDMH-N_2H_2	5000	100	1	182 sec	No erosion

Miscellaneous

Incorporation of an Invar 36 attachment ring to the slip-cast fused-silica Trailblazer nosecap was described by General Dynamics/Pomona. This alloy was selected because of its thermal-expansion fit with fused silica. The metal-ceramic attachment was made using EC-1290 (3M) primer and 901/B-1 epoxy (Shell Chemical). An assembled nosecap/attachment ring passed mechanical-vibration and thermal-cycling tests without failure.

In a program to develop power conductors to function reliably up to 2000 F under all aerospace environmental conditions, Melpar fabricated and evaluated prototype 22-gage and 12-gage power conductors. These used rhodium power wires, magnesium oxide insulation, platinum sheathing, and alumina end seals. The conductor systems maintained their electrical integrity through a variety of environmental tests, including vibration, mechanical shock, acceleration, humidity, vacuum, and nuclear radiation. The wires were operated successfully at 2000 F. Rated current was determined and assigned as 10 amperes for 22-gage and 60 amperes for 12-gage conductors. The conductors passed the final cyclic test of carrying rated current at room temperature for 2 hours, at high vacuum for 25 hours, and at a reduced pressure at 2000 F for 3 hours.

Engineering behavior of electrophoretic Cr-Ti-Si coated columbium alloy (Cb-752 and C-129Y) fasteners was reviewed by Vitro. Oxidation behavior in static air and in dynamic 200 ft/sec air was:

Test Temp, F	Average Life, hours: Static Air	Dynamic Air
2200	65	3.3
2600	10	0.8
2800	0.5	0.2

In tensile and shear tests, coated threaded bolts exhibited markedly lower strength than uncoated bolts at -320 F, but strengths at higher temperatures (RT and 600 F) were comparable. Tension-tension fatigue behavior was also evaluated. Oxidation-compatibility tests between the Vitro-coated fasteners and TRW- and Pfaudler-coated columbium-alloy specimens or TD nickel showed (1) good compatibility of coated fasteners with TRW-coated hardware, (2) poor compatibility with TD nickel, and (3) inconclusive results with Pfaudler-coated hardware because of limited life of same. Fiberfrax washer separation was effective in improving compatibility with TD nickel.

EVALUATION TECHNIQUES

Thermal-Testing Facilities

A report from NASA-Marshall summarized the status of the 18,000-kw plasma facility. This is a hyperthermal "blow-down"-type wind tunnel which can simulate the reentry environment of missile nose cones in the altitude range from 400,000 to 100,000 feet. Its peak output involves transient-state operation limited by vacuum reservoir capacity and power capability. One to six plasma generators are used to heat the gas. The plasma column may be 20 inches in diameter by 16 to 32 feet long, and supports temperatures between 8,500 and 89,000 F. The facility is still under development with some of the equipment and instrumentation yet to be installed. This facility was built primarily as a device to support applied research in very high-speed flight. Interested potential users of this facility may contact Dr. T. A. Barr, Jr., Chief Plasma Physics Branch, Attn: AMSMI-RRP, Bldg. 4762, Redstone Arsenal, Alabama.

The University of Dayton Research Institute has developed a facility for conducting bench tests of rocket-nozzle materials. This is a contained 150-kw arc plasma with a multicomponent injection system which feeds from a modest-pressure mixing chamber through a scale nozzle of the test material. The effluent is scrubbed, washed, neutralized, and exhausted to atmosphere or drain. Temperature and

chamber pressure are monitored, and continued observation of the test piece is permitted. An evaluation of the compatibility between nozzle materials and typical propellant exhaust species is the objective of this facility. Tests involving tungsten, graphite, and various ablative nozzle materials were described. Figure 9 illustrates data obtained on ATJ graphite with CO_2 injection at three test temperatures. By varying nozzle design to extend the throat length, longer times under isobaric conditions can be achieved. It was pointed out that this test is not generally intended to directly simulate firing tests; rather it supplements existing evaluation procedures.

Facilities, calibration, operation, and test specimen design for conducting low-heat-flux tests using radiant energy from banked heat lamps, and also high-heat-flux tests using a plasma splash test were documented in the report by researchers at General Dynamics/Fort Worth.

Quality Control

As a result of continued development of resin-impregnated porous-ceramic bodies, Martin-Baltimore described engineering evaluation procedures and manufacturing capabilities of porous zirconia bodies from various sources. A simple quality-control test to grade the suitability of porous ZrO_2 blocks for manufacturing operations, involves pressing a flat-faced steel cylinder into the surface of the block to a depth of 60 mils, while monitoring the load-versus-penetration response. Blocks that were easily machinable to good tolerances displayed relatively smooth load-penetration curves, and blocks of unacceptable machinability showed far more irregular load-penetration curves. This behavior appeared related to the cell structure of the porous bodies.

Martin-Baltimore's Advanced Structural Concepts Experimental Program (ASCEP) has treated various aspects of superalloy and refractory-metal technology. Of particular importance was the development of nondestructive test methods for honeycomb sandwich structures. A Sperry SIMAC Ultrasonic Recording System is used for either pulse-echo or through transmission to define faulty core-to-skin joints. Panels are immersed in a water bath, and the surface is 100 percent inspected by an automatic scanning bridge. Response is documented by a plan-view recorder with a recording ratio of 1:1.

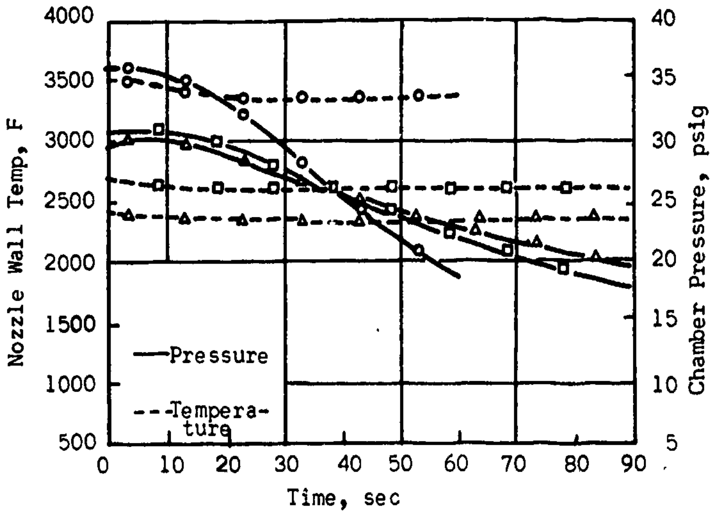

FIGURE 9. TYPICAL PRESSURE-TEMPERATURE-TIME HISTORIES OF ATJ GRAPHITE NOZZLE SPECIMENS EXPOSED TO AN N_2-CO_2 EFFLUENT AT INITIAL TEMPERATURES OF 2400, 2700, AND 3500 F (Dayton Research Institute)

Miscellaneous

Bell Aerosystems described a method for direct laboratory evaluation of brittle materials for possible application as leading-edge members of glide-reentry vehicles. Previous reports to the Refractory Composites Working Group described preliminary evaluation and development of fabrication processes for Boride Z, from which simulated, scaled-down leading-edge segments were fabricated. In their recent studies, Bell conducted thermal exposures of the shaped components in duplicate. The heat source was a radiant ceramic heated by oxyacetylene combustion; downstream air augmentation provided a dynamic, but subsonic environment. Heating and cooling programs in 30-minute cycles were designed to provide thermal response of the test shapes such as expected during ascent and descent phases of varying severity. Of principal importance was the result that failures of the test shapes occurred under test conditions that closely matched predictions based on knowledge of physical and mechanical behavior of the Boride Z test material. It was concluded that a direct evaluation technique has been developed to assess economically the suitability of brittle refractory nonmetallic materials for hypersonic leading-edge applications. The technique relates test conditions to mission parameters, thereby providing a quantitative indication of the potential usefulness of materials tested.

The importance of evaluation procedures in ranking the behavior of coated metal systems was emphasized by Chromalloy. Specifically, regarding the merits of static and dynamic tests related to the evaluation of hardware systems for jet engines, it was stated that "protective systems when exposed to service or simulated service environment may... perform with different orders of merit from those determined in simple oxidation". For this reason, developments at Chromalloy are based primarily on results of testing in a "Gas Stream Erosion Rig" which was described.

The Space Technology Laboratories of TRW described a program to develop analytical means for predicting the thermal-shock response of materials to various environments. Included are analytical parameters for heat transfer, stress, strain, geometry of the part, externally applied forces, and materials' behavior (elastic and plastic deformation regimes versus temperature, anisotropy, etc.). Test data are generated on cylindrical specimens heated on the ID by an electron beam which can generate up to 10,000 Btu/ft^2-sec (sufficient to effect ID melting of tungsten in less than 1 second). Thus far, both extruded and hot-pressed tungsten, several metallic alloys, and nonmetallic specimens have been tested. Results thus far agree semiquantitatively with analytical procedures, and additional analytical refinements are expected to further improve ability to broadly predict thermal-shock behavior of materials. An interesting sidelight is that repeated subfailure thermal cycling appears to improve the thermal-shock resistance of plastically deformable materials by inducing

residual compressive stresses in regions backing up the internal surface (i.e., by causing compressive plastic flow at the ID).

The importance of vaporization processes in the response of refractory materials to environments was treated in the presentation by Arthur D. Little, Inc., workers. Both thermodynamic and kinetic aspects were considered. Examples involving vaporization from the surface of a solid system to the gaseous environment, and reaction and evaporation at and from an interior interface in a heterogeneous (e.g., coated) solid body were presented. Factors influencing the kinetics of volatilization were discussed; such factors determine whether the kinetics are reaction controlled (e.g., in the case of ample supply of reactants), or diffusion controlled (e.g., in the case where a gaseous oxidation product forms a boundary layer to inhibit access of one reactant to the reaction surface). Predictions of limiting conditions for diffusion-controlled oxidation of tungsten, graphite, and iridium were made from a theoretical foundation. These predictions were found to be in reasonable agreement with experimental results.

The National Bureau of Standards is developing emittance standards and preferred methods for measuring emittance to temperatures of 6000 F under Air Force funding. Interested persons are invited to contact either of the following people for additional details:

U. S. Department of Commerce
National Bureau of Standards
Washington, D. C.

Attention Mr. J. C. Richmond

Air Force Materials Laboratory
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Wright-Patterson Air Force Base, Ohio

Attention Mr. D. F. Stevison
MAAE

APPENDIX A

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APPENDIX B

INDEX OF PAPERS*

	Page
Aeronutronics Division of Philco Corporation A. M. Saul, W. L. Smallwood, and H. M. Blaes II "An Analysis of the Chemical Behavior of Reinforced Resins in Some Propellant Systems of Current Interest"	13
Allison Division of GMC D. G. Miller, R. H. Singleton, and A. V. Wallace "Metal Fiber Reinforced Ceramic Composites"	9
American Radiator and Standard Sanitary Corporation G. P. K. Chu "Silicide Coatings on Tantalum and Co-Deposition of TaC and $TaSi_2$ on Tantalum"	5
Arthur D. Little, Inc., and Manlabs, Inc. J. B. Berkowitz-Mattuck and L. P. Kaufman "The Influence of Vaporization Processes on Oxidation"	16
Atomics International Division of North American Aviation, Inc. A. K. Smalley "BeO Single Crystal Filaments: Their Growth and Their Potential as Reinforcement in Composite Structures"	10
Avco Corporation J. T. Smith "Refractory Composites for Thermal Protection"	2
Battelle Memorial Institute--Northwest R. K. Robinson and P. L. Farnsworth "Tungsten Fiber Reinforced Nickel Composites"	8
Bell Aerosystems Company, a Division of Bell Aerospace Corporation, a Textron Co. F. M. Anthony "A Direct Evaluation Technique for Brittle Leading Edge Materials"	15
The Boeing Company "Advances in Refractory Alloy Coatings Technology Resulting from the X-20 Program"	3
The Boeing Company J. M. Gunderson, C. A. Krier, and F. H. Simpson "Refractory Composite Research and Developments"	3
Chromalloy Division of Chromalloy Corp. A. Noetzel and M. Epner "Activities in the Development of Refractory Composites"	7,15
Cincinnati Testing Laboratories C. F. Zapf "Ceramic Reinforcements for Composites"	11
Continental Aviation and Engineering Corp. T. A. Weidig "Intermetallic Materials at Temperatures of 2000 F to 3000 F"	1
Dayton Research Institute (University of) J. C. Wurst and D. A. Gerdeman "Screening of Candidate Rocket Nozzle Materials"	14
General Dynamics/Fort Worth M. S. Howeth "Ablation Composites Evaluation"	2,15
General Dynamics/Pomona S. C. Colburn and R. L. Hallse "Strength of Slip Cast Fused Silica"	2,14
General Technologies Corporation R. G. Shaver and J. C. Withers "Reinforced Metal Composites"	8,13
General Telephone and Electronics Laboratories J. Brett and L. L. Seigle "Experimental Study of Factors Controlling the Effectiveness of High-Temperature Protective Coatings for Tungsten"	4
Georgia Institute of Technology J. N. Harris "Felted Ceramics and Pre-Stressed Slip Cast Fused Silica"	2,9
Harvey Engineering Laboratories L. W. Davis "Fabrication of Fiber Metal Composites"	8
IIT Research Institute S. A. Bortz "A Review of Current Refractory Composite Research in Ceramics"	3,9,11, 13
IIT Research Institute V. L. Hill and J. J. Rausch "Current Status of Coatings for the Protection of Tantalum Above 3500 F"	4
LTV-Vought Aeronautics Division W. L. Aves and G. Bourland "Research and Development in Coating Application Processes for Refractory Metals"	6
LTV-Astronautics Division B. A. Forcht, I. E. Harder, and R. K. Carlson "Reinforced Pyrolyzed Plastics"	9
LTV-Vought Research Center R. F. Wehrmann "Evaporated Carbon Coatings"	1
Lockheed Missiles and Space Company C. M. Packer, R. A. Perkins, A. W. Lavendel, and A. G. Elliott "Oxidation-Resistant Coatings for Refractory Metals"	6

*Numbers following name of paper are numbers of the pages on which the reference is mentioned.

	Page
Marquardt Corporation B. A. Webb "Materials Research Activities"	2,3,7, 11,13
The Martin Company, Baltimore Division E. L. Strauss "Studies of Advanced Refractory Composites Concepts for Structural and Heat Shield Applications"	6,13, 15
McDonnell Aircraft Corporation J. D. Culp, B. G. Fitzgerald, and J. C. Sargent "Recent Refractory Metal Coating Activities"	4,6
Melpar, Inc. K. M. Zwilsky N. Fuschille, H. Hahn, and M. L. Gimpl "2000 F Power Conductors for Aerospace Applications"	14
Metco, Inc. H. S. Ingham, Jr., and F. N. Longo "Flame Sprayed Molybdenum"	11
Narmco Research and Development Division, Whittaker Corporation R. A. Long and F. A. Barr "Narmco's Activities in Refractory Composite Materials"	11,13
NASA-Langley Research Center G. R. Wichorek and B. A. Stein "Preliminary Results of a Study of Coated Ta-10W Sheet for Heat-Shield Applications"	6
NASA-Lewis Research Center S. J. Grisaffe "Shear Bond Strength of Alumina Coatings"	7
NASA-Marshall Space Flight Center T. A. Barr, Jr., C. M. Cason, R. F. Mayo, J. J. Ehrlich, L. L. Dickerson, and T. G. Roberts "The Development of the Amicon 18,000 KW Hyperthermal Test Facility"	14
Norton Exploratory Research Division L. R. Allen "Refractory Composites"	10
Norton Company, Research and Development Department W. M. Wheildon "Status of Rokide Coating System and Summary of Hot Pressing Capabilities"	2,11
Oak Ridge National Laboratory R. L. Heestand, J. I. Federer, F. H. Patterson, and C. F. Leitten, Jr. "Summary of Thermochemical Deposition Studies"	11

	Page
Pfaudler Company G. J. Dormer, B. S. Payne, E. G. Pike, J. B. Whitney, and J. Zupan "Research in Protective Coatings for Refractory Metals"	6
Pratt & Whitney Aircraft, Division of United Aircraft Corporation H. A. Hauser and A. J. Moses "Some Properties of Chromium-Magnesia Alloys"	3
Solar, International Harvester Company A. R. Stetson "An Analysis of the (Cr-Ti)-Si Coating Chemistry and Modification for the Protection of Columbium-Base Alloys"	6
Sylvania Sylcor Division, GT&E L. Sama, S. Priceman, B. Reznik, D. Bracco, and P. Tublin "Development of Oxidation Resistant Coatings for Refractory Metals"	3
Thompson Ramo Wooldridge Equipment Laboratories D. N. Crump and E. A. Steigerwald "Throat Inserts for Ablative Thrust Chambers"	13
Thompson Ramo Wooldridge Space Technology Laboratories J. R. Bohn "Thermal-Shock Characteristics of Refractory Materials"	15
Union Carbide Corporation, Carbide Products Division H. F. Volk and J. M. Criscione "Iridium Coatings for the Protection of Graphite From Oxygen at High Temperatures"	7
United Technology Center, Division of United Aircraft Corporation M. A. Schwartz and T. A. Greening "Refractory Composites Work"	13
Vitro Laboratories S. Grand "High Temperature Coatings for Tantalum-Base Alloys"	5
Vitro Laboratories M. Ortner "Electrophoretic Coatings for Refractory Metal Structural Fasteners"	14

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13. ABSTRACT

This memorandum summarizes information on refractory materials and composites as presented at the Tenth Meeting of the Refractory Composites Working Group, in Atlanta, Georgia, on April 12-14, 1965. This memorandum is based on 48 papers covering a wide variety of subjects ranging from basic studies on oxidation mechanisms to the development of specific pieces of hardware. The papers are reviewed and discussed briefly within the framework of the following four broad areas: materials technology, process technology, specific hardware applications, and evaluation techniques. Included in the section on materials technology are discussions dealing with bulk refractory materials, coated-metal systems, and fiber-reinforced composites. Hot spraying, chemical vapor deposition, and other areas of manufacturing technology are discussed in the section on process technology. The specific hardware applications cover rocket-motor components, nose caps, electrical conducters, and fasteners. (Author)

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